Predicting the Service-Life of Concrete Structures Exposed to Chemically Aggressive Environments

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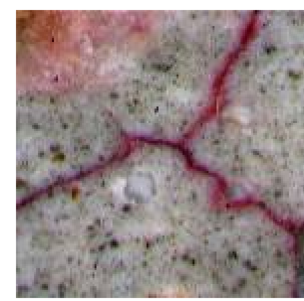
Materials Service Life
Laval University

CEMENTITIOUS MATERIALS FOR WASTE TREATMENT, DISPOSAL, REMEDIATION & DECOMMISSIONING WORKSHOP

Savannah River Site, Aiken South Carolina
December 12-14, 2006

ΣSUMMA
Numerical Model for Concrete Durability

Concrete degradation



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Numerical Model for Concrete Durability

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Multi-ionic model

The transport of ions in **STADIUM®** is modeled with the extended Nernst-Planck equation with an advection term:

Mass conservation equation:

$$\frac{\partial (w c_i)}{\partial t} + \mathrm{div}(j_i) = 0$$

Flux of ions (1D):

$$j_i = -\underbrace{w D_i \frac{\partial c_i}{\partial x}}_{\text{diffusion}} - \underbrace{w \frac{D_i z_i F}{RT} c_i \frac{\partial \psi}{\partial x}}_{\text{electrical coupling}} - \underbrace{w D_i c_i \frac{\partial \ln \gamma_i}{\partial x}}_{\text{chemical activity}} - \underbrace{D_w c_i \frac{\partial w}{\partial x}}_{\text{advection}}$$

Variables:

- **Concentrations** c_i
- **Diffusion potential** ψ
- **Water content** w
- **Temperature** T

Multi-ionic model

To complete the system of equations, the following relationships are considered:

Poisson:

$$\tau \frac{d}{dx}\left(w \frac{d\psi}{dx}\right) + \frac{F}{\epsilon} w \left(\sum_{i=1}^{N} z_i c_i\right) = 0$$

Richards:

$$\frac{\partial w}{\partial t} - \frac{\partial}{\partial x}\left(D_w \frac{\partial w}{\partial x}\right) = 0$$

Heat conduction:

$$\rho C \frac{\partial T}{\partial t} - div \; (k \mathrm{grad} T) = 0$$

The system of equations is solved using the finite element method:

- **11 unknowns: 8 x c_i + w + ψ + T**
- **11 equations: 8 conservation + Poisson + Richards + Heat**

Multi-ionic model

The chemical reactions are modeled according to dissolution/precipitation equilibrium relationships:

Dissolution/precipitation:

$$K_m = \prod_{i=1}^{N} c_i^{\nu_{mi}} \gamma_j^{\nu_{mi}}$$

Portlandite:

$$K_{\mathrm{CH}} = \gamma_{\mathrm{Ca}} \gamma_{\mathrm{OH}}^2 [\mathrm{Ca}][\mathrm{OH}]^2$$

In the case of chlorides, the formation of Friedel's salts is modeled according to an ionic exchange relationship:

- **Friedel's salts formation:**

$$\underbrace{(\mathrm{AFm^+\text{-}SO_4^{2-}})}_{\text{Monosulfates}} + 2\mathrm{Cl^-} \rightarrow \underbrace{(\mathrm{AFm^+\text{-}2Cl^-})}_{\text{Friedel's salt}} + \mathrm{SO_4^{2-}}$$

- **Relationship:**

$$K = \frac{\{\mathrm{Cl}\}^2}{\{\mathrm{SO4}\}} \frac{[\mathrm{AFm}_{SO4}]}{[\mathrm{AFm}_{Cl}]}$$

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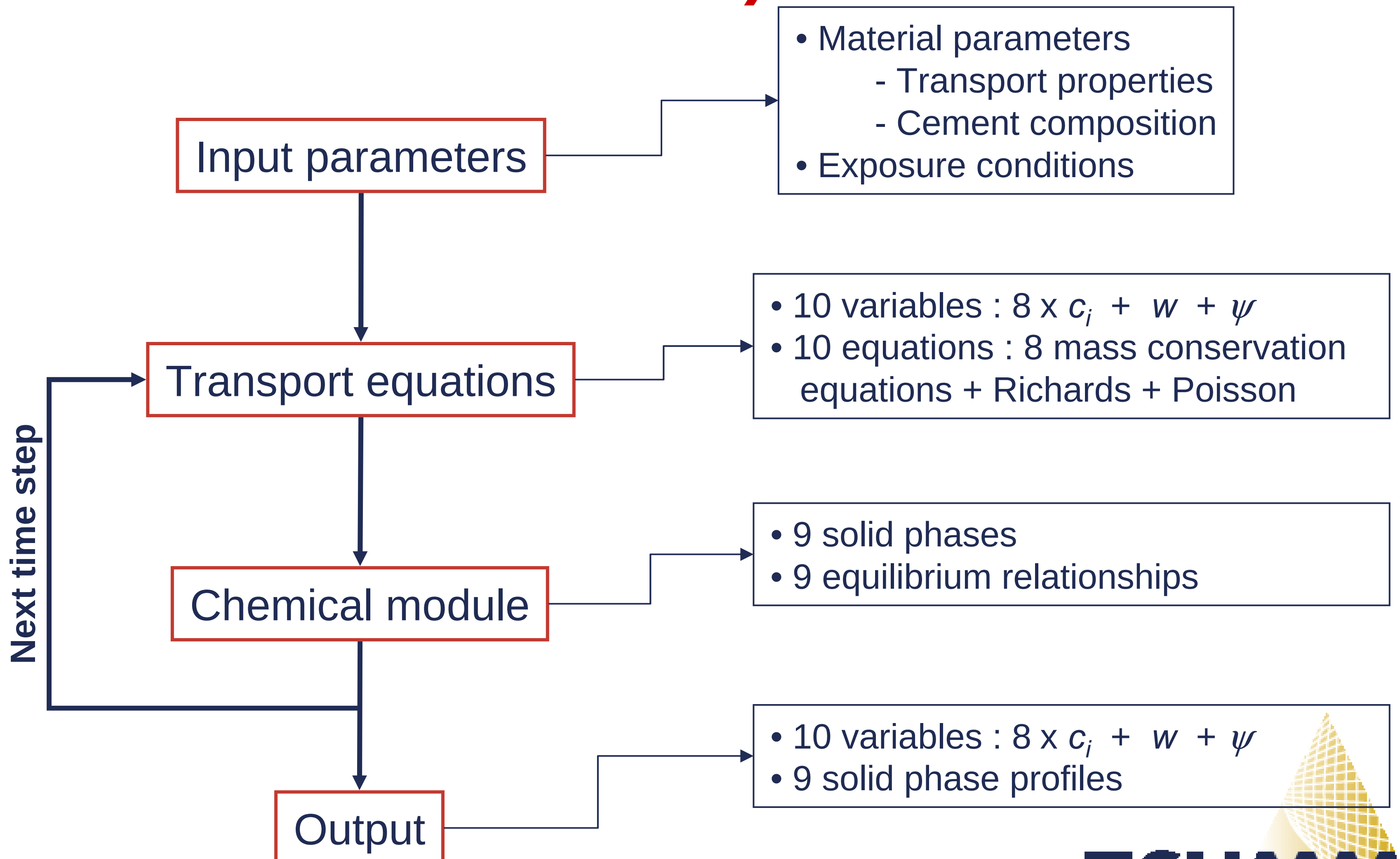
Operator-splitting algorithm
(Isothermal case - SNIA)



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Numerical Model for Concrete Durability

Multi-ionic model

To bring the solution back to equilibrium at one node, the following non-linear system of equations is solved:

$$K_{CH} = \gamma_{Ca}\,\gamma_{OH}^{2}\,(Ca° + X_{CH} + 6X_{Aft} + X_{Gyp} + \ldots)\,(OH° + 2X_{CH} + 4X_{Aft} + \ldots)^{2}$$

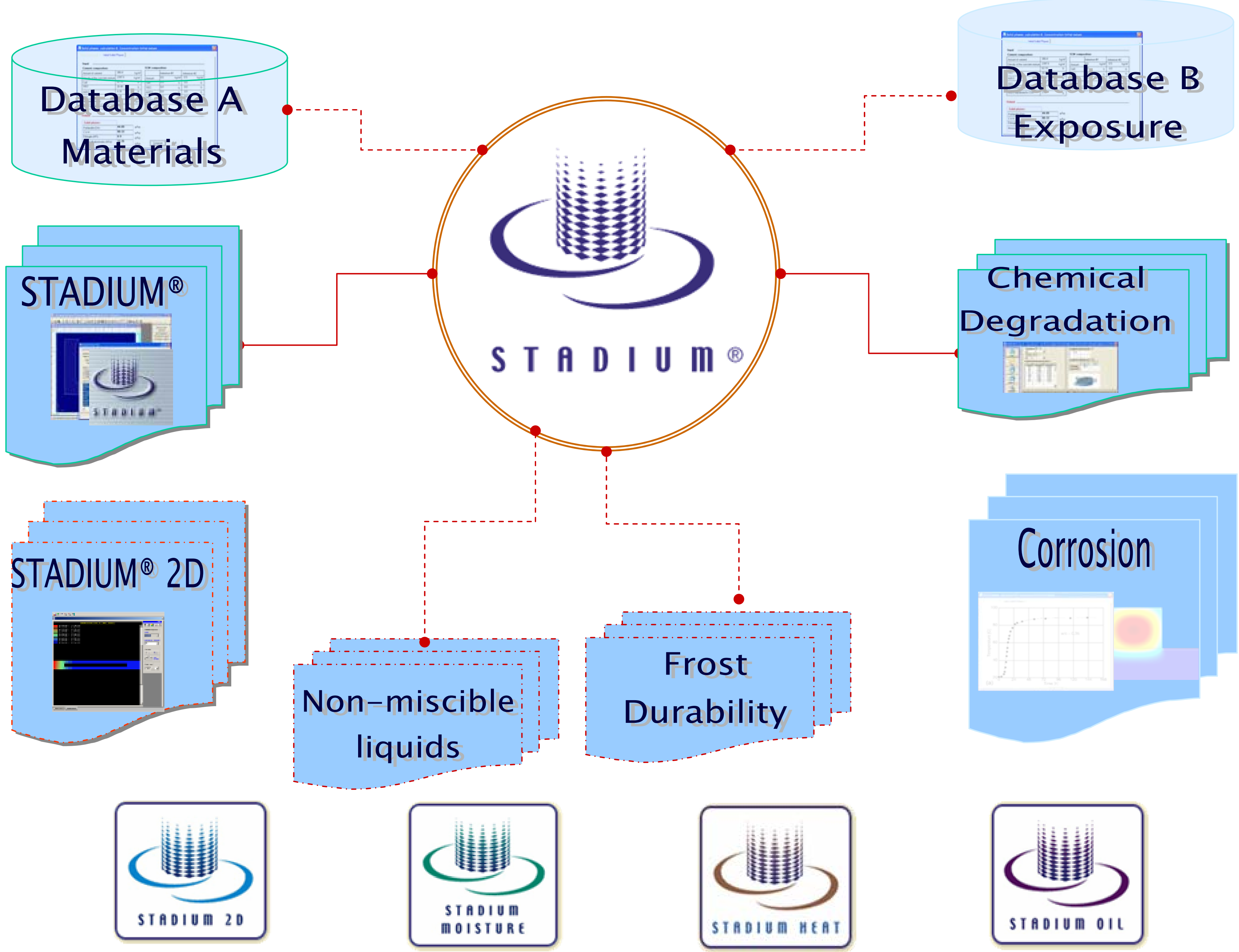
$$K_{Gyp} = \gamma_{Ca}\,\gamma_{SO4}\,(Ca° + X_{CH} + 6X_{Aft} + X_{Gyp} + \ldots)\,(SO_4° + 3X_{Aft} + X_{Gyp} + \ldots)$$

$$\vdots \qquad\qquad \vdots \qquad\qquad \vdots$$

X_i = amount of solid i dissolved or formed
C° = concentration before equilibrium

Numerical method: Newton-Raphson

Numerical Model for Concrete Durability



Database A
Materials
Database B
Exposure
STADIUM®
STADIUM®
Chemical
Degradation
STADIUM® 2D
Corrosion
Non-miscible
liquids
Frost
Durability
STADIUM 2D
STADIUM
MOISTURE
STADIUM HEAT
STADIUM OIL

Input parameters

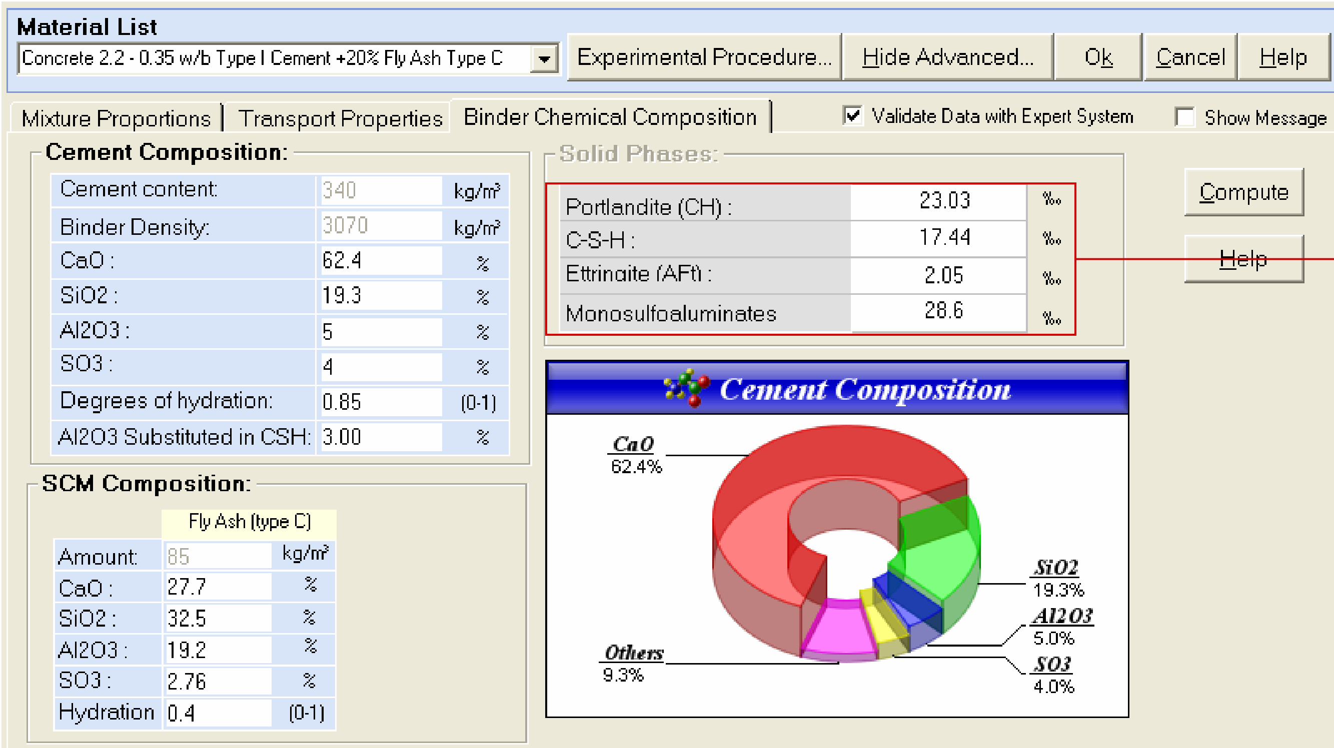
In order to run the model, one needs to generate information on the following properties:

- Mixture characteristics
- Binder composition
- Porosity
- Pore solution
- Diffusion coefficients (formation factor)
- Water diffusivity

The other parameters are either physical constants or properties that have a relatively weak influence on the output:

- F, R, z_i, …
- Thermal properties: k, C

Cement chemistry



$$\frac{\Gamma_{\mathrm{Ca}}}{\Gamma_{\mathrm{CH}}} S_{\mathrm{CH}} + 1.65\frac{\Gamma_{\mathrm{Ca}}}{\Gamma_{\mathrm{csh}}} S_{\mathrm{csh}} + 6\frac{\Gamma_{\mathrm{Ca}}}{\Gamma_{\mathrm{AFt}}} S_{\mathrm{AFt}} + 4\frac{\Gamma_{\mathrm{Ca}}}{\Gamma_{\mathrm{AFm}}} S_{\mathrm{AFm}} = 10\ \mathrm{CaO}\frac{\Gamma_{\mathrm{Ca}}}{\Gamma_{\mathrm{CaO}}}$$

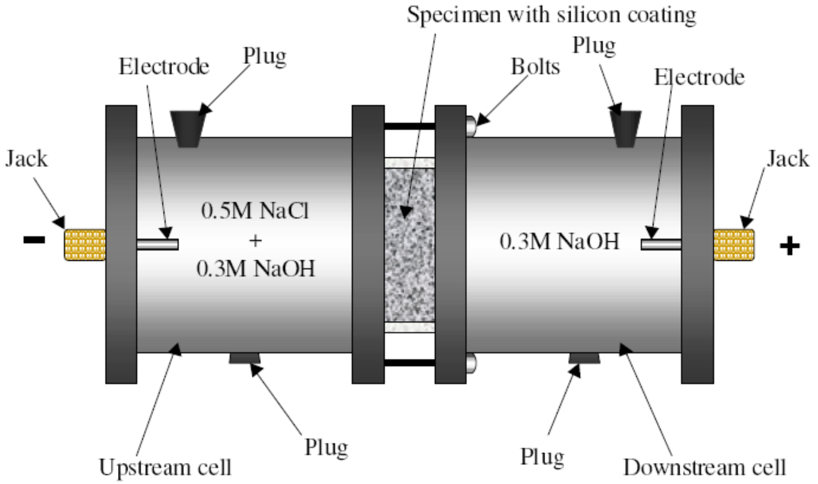
$$\frac{\Gamma_{\mathrm{Si}}}{\Gamma_{\mathrm{csh}}} S_{\mathrm{csh}} = 10\ \mathrm{SiO_2}\frac{\Gamma_{\mathrm{Ca}}}{\Gamma_{\mathrm{SiO_2}}}$$

$$2\frac{\Gamma_{\mathrm{Al}}}{\Gamma_{\mathrm{AFt}}} S_{\mathrm{AFt}} + 2\frac{\Gamma_{\mathrm{Al}}}{\Gamma_{\mathrm{AFm}}} S_{\mathrm{AFm}} + 2\xi_{\mathrm{Al2O3}}\frac{\Gamma_{\mathrm{Al}}}{\Gamma_{\mathrm{Al2O3}}} S_{\mathrm{csh}} = 10\ \mathrm{Al_2O_3}\frac{2\Gamma_{\mathrm{Al}}}{\Gamma_{\mathrm{Al2O3}}}$$

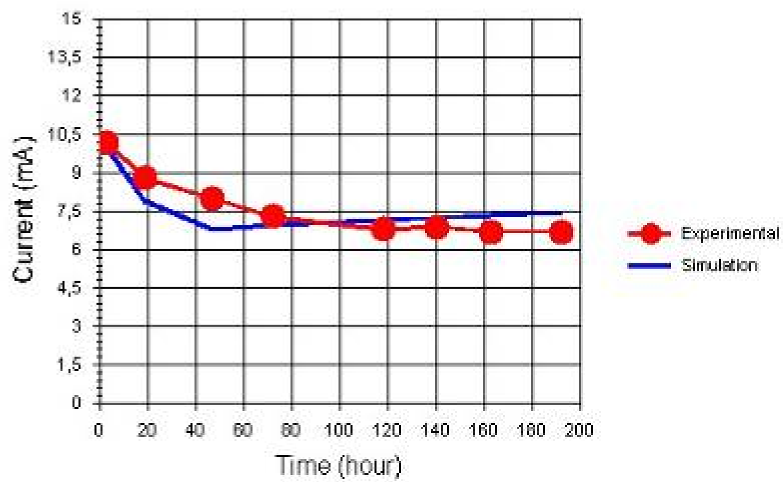
$$3\frac{\Gamma_{\mathrm{S}}}{\Gamma_{\mathrm{AFt}}} S_{\mathrm{AFt}} + \frac{\Gamma_{\mathrm{S}}}{\Gamma_{\mathrm{AFm}}} S_{\mathrm{AFm}} = 10\ \mathrm{SO_3}\frac{\Gamma_{\mathrm{S}}}{\Gamma_{\mathrm{SO3}}}$$

Diffusion coefficients

Experimental procedure:



$$I_c^{num} = SF \sum_{i=1}^{N} z_i j_i$$



Evaluation of the diffusion coefficients for all ionic species:

- **OH**
- **Na**
- **K**
- **SO4 ...**

Diffusion coefficients

ASTM Type I

w/c = 0.5 – Cure = 18 m.

Test Condition		
Solution	V/mm	τ
NaCl – 0.5 M	0.4	35.4
NaCl – 0.5 M	0.2	38.5
NaCl – 0.1 M	0.4	39.0
Na_2SO_4 – 0.2 M	0.4	41.0

Variation = ± 14%

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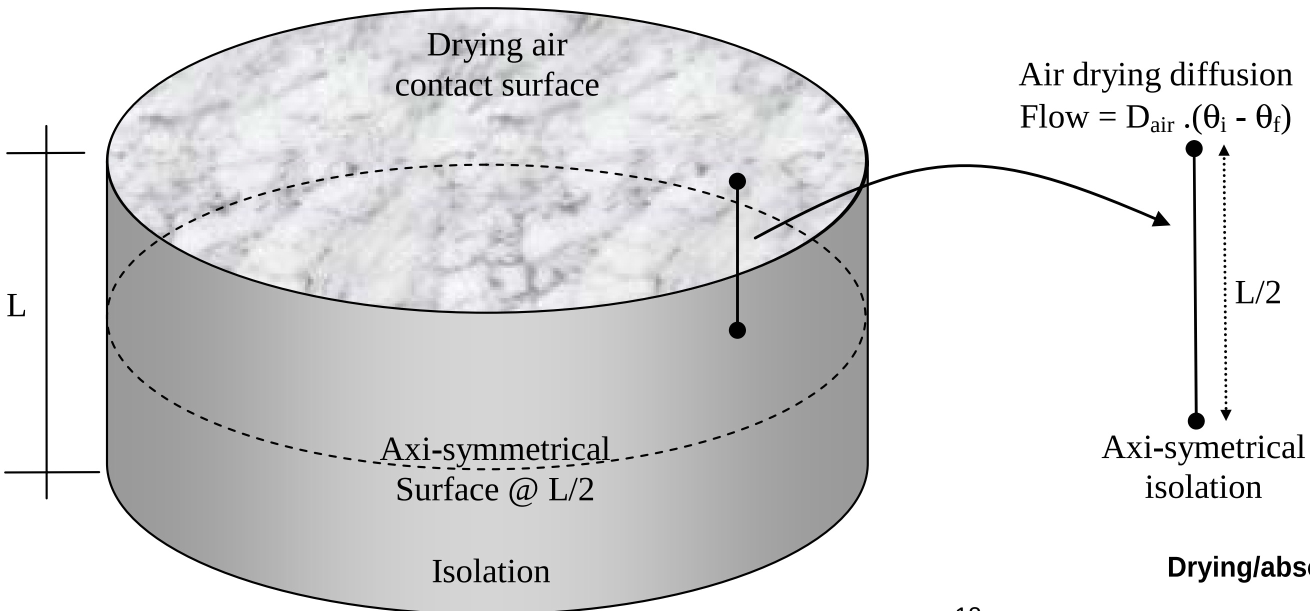
Samson et al. (2003) Materials and Structures, (36) 156

Water diffusivity

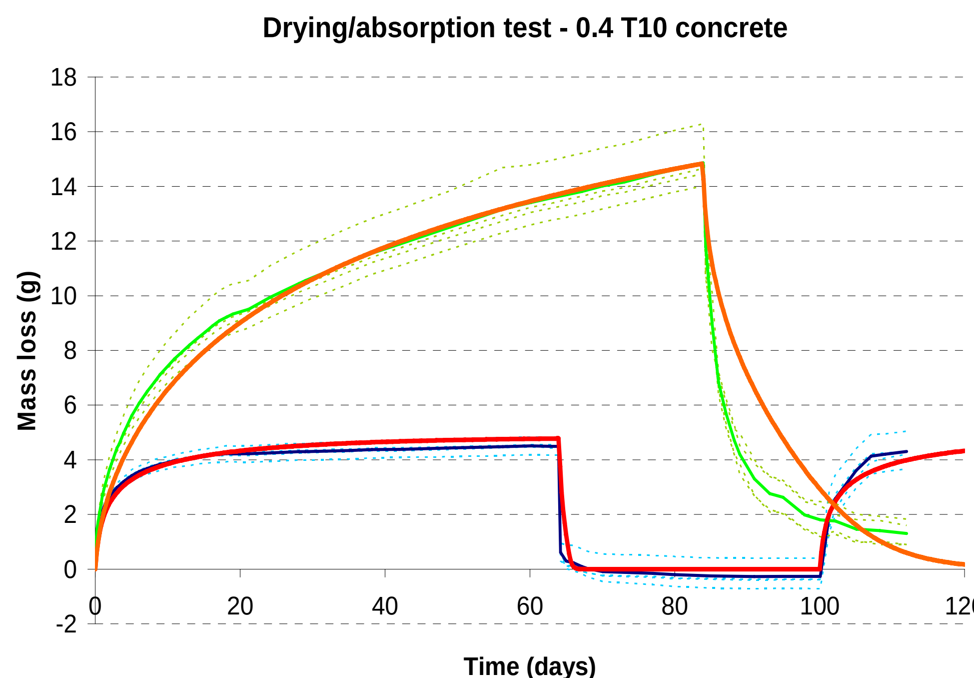


$$\begin{cases} \theta(x,0) = \phi \\ \left.\dfrac{\partial \theta}{\partial x}\right|_{x=0} = 0 \\ D(\theta)\left.\dfrac{\partial \theta}{\partial x}\right|_{x=L/2} = D_{air}(\phi - \theta_f) \end{cases}$$

$$D = D_0 \exp(Bw)$$

B = 80 for all

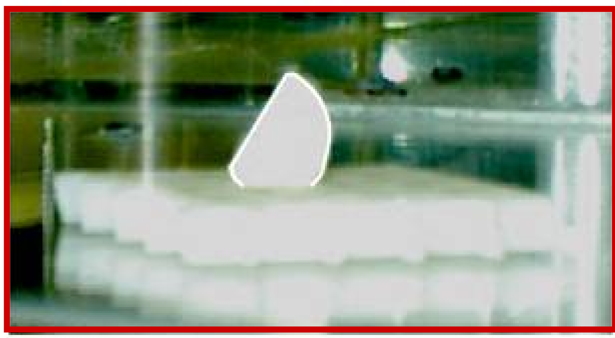
$D_0 = 1.5 \times 10^{-14}$ (w/c = 0.45)
$D_0 = 15 \times 10^{-14}$ (w/c = 0.75)



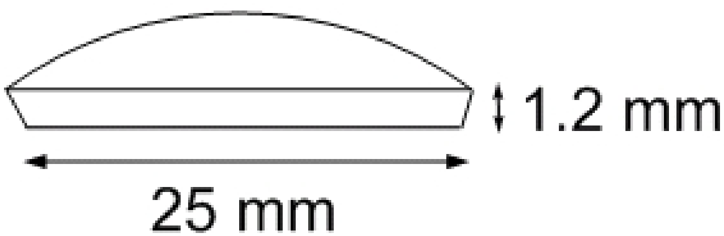
Exposure conditions

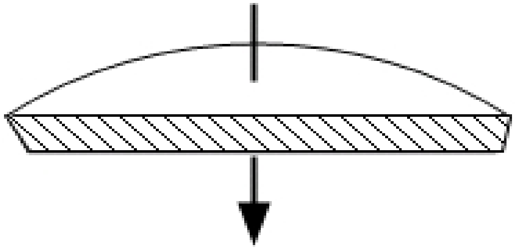
Experimental validation

Thin C_3S slices



25-L Reservoir

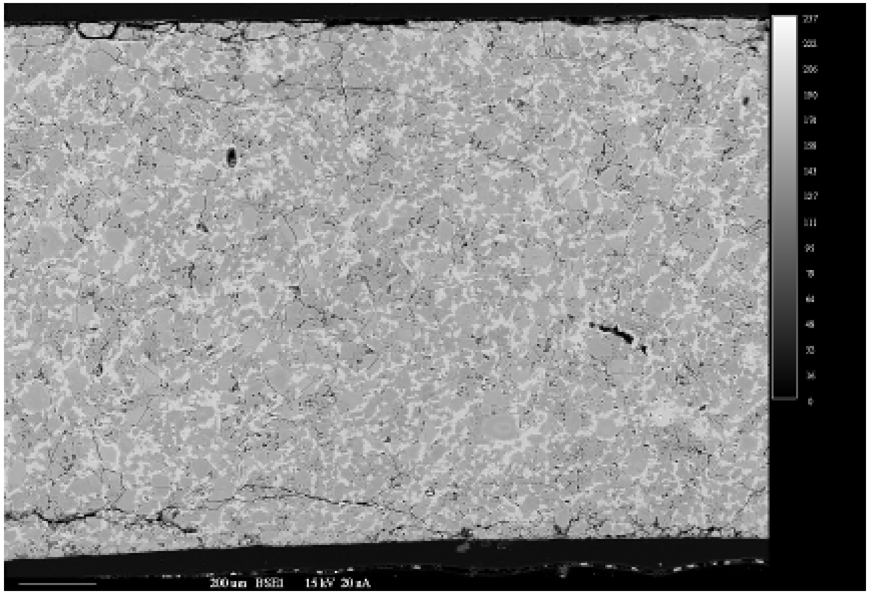




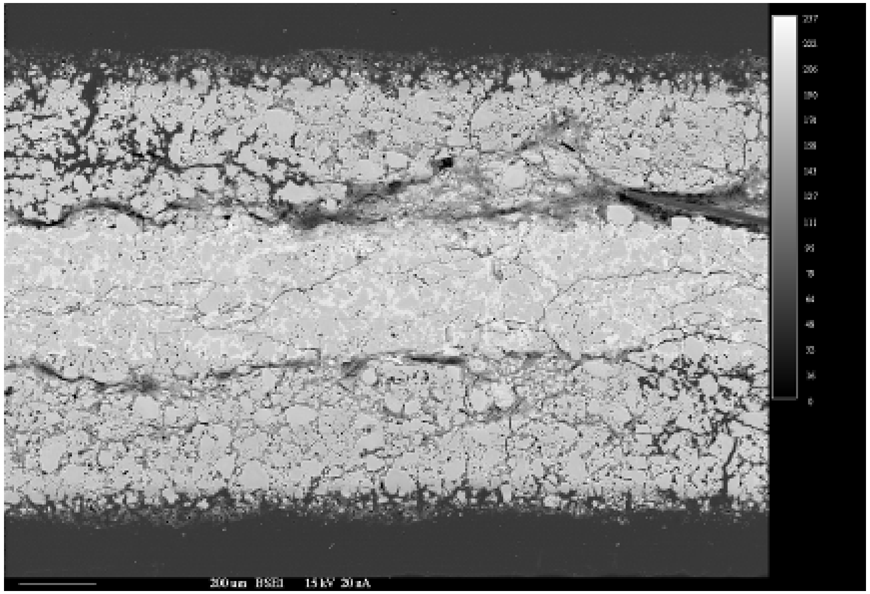
Validation - Leaching

Degradation analyses

Sound C_3S paste



Leached C_3S paste

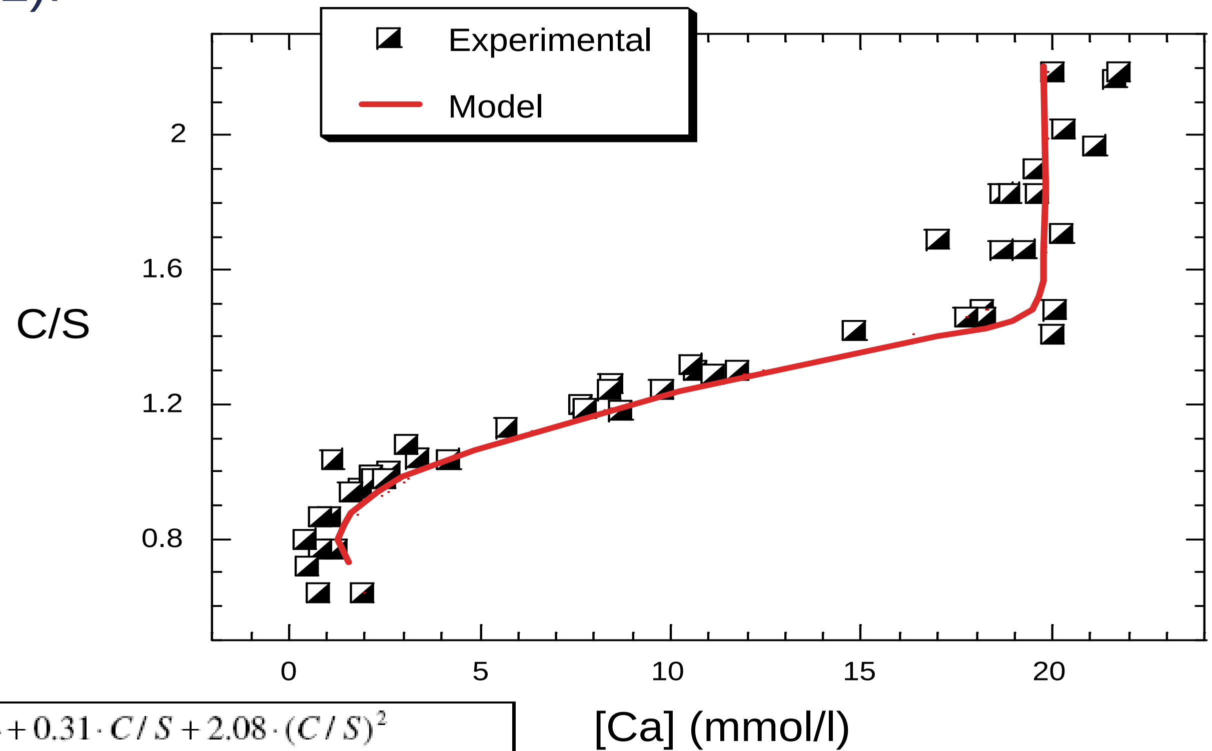


Initial Porosity = 50% $\tau = 35.2$

Modeling - Leaching

The C-S-H decalcification modeling is based on Berner's approach (1992):

Ca^{2+}
$Ca(OH)^{+}$
H_4SiO_4
$H_3SiO_4^{-}$
$H_2SiO_4^{2-}$

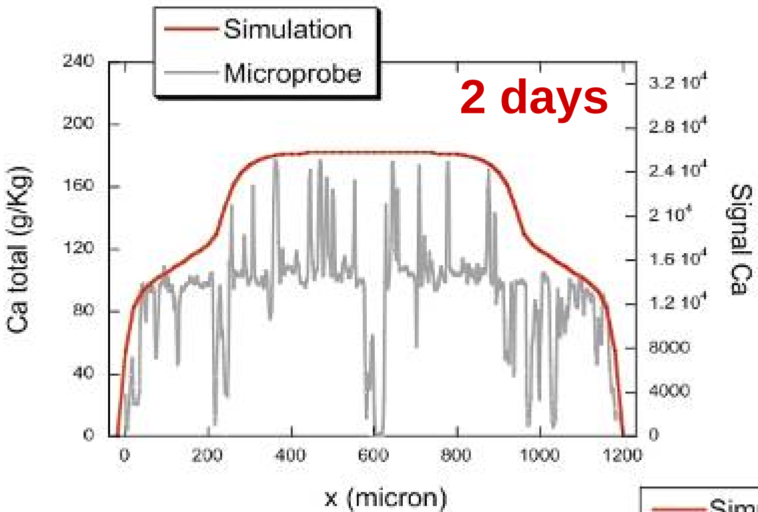


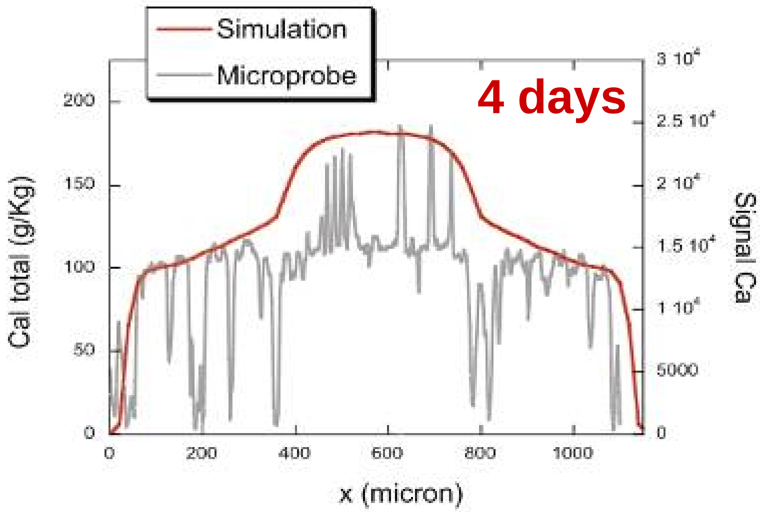
$C/S \le 0.7$	$pK_{SiO2} = 2.74 + 0.31 \cdot C/S + 2.08 \cdot (C/S)^2$ $pKcsh = 7.50$
$0.7 \le C/S \le 1.5$	$pKcsh = 5.29 + 3.01 \cdot C/S - 0.51 \cdot (C/S)^2$ $pK_{Ca(OH)2} = 18.54 - 16.58 \cdot C/S + 5.15 \cdot (C/S)^2$
$C/S \ge 1.5$	$pKcsh = 8.60$ $pK_{Ca(OH)2} = 5.18$

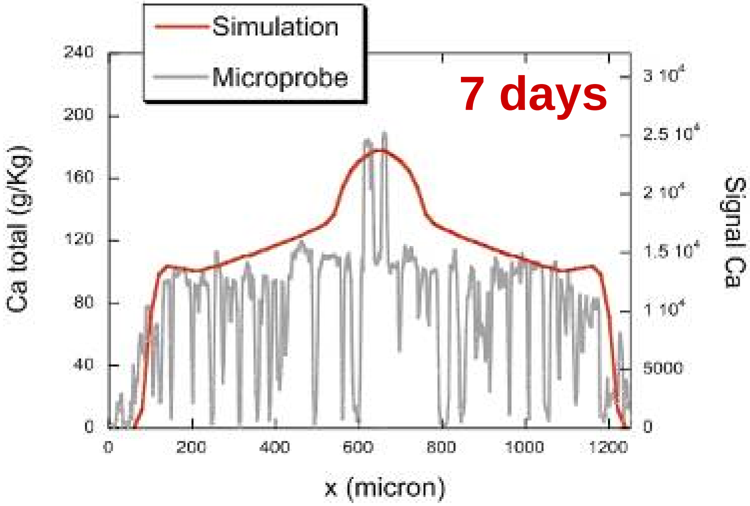
Validation - Leaching

Thin C_3S slices (w/c: 0.5) – Pure water

Calcium profiles



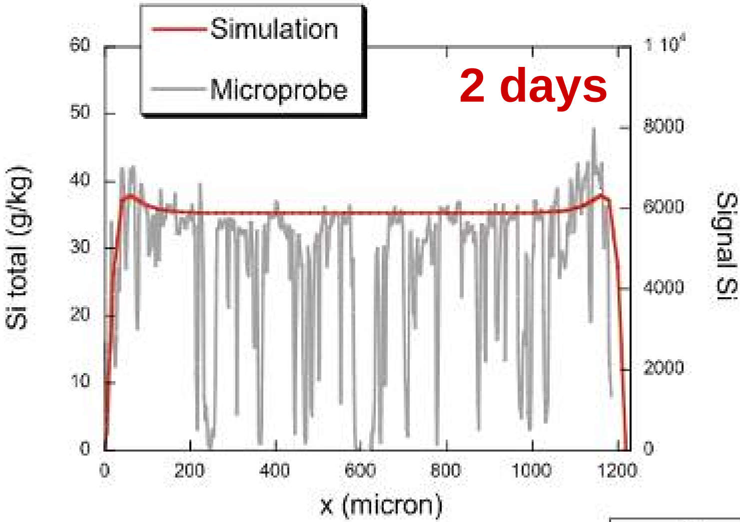


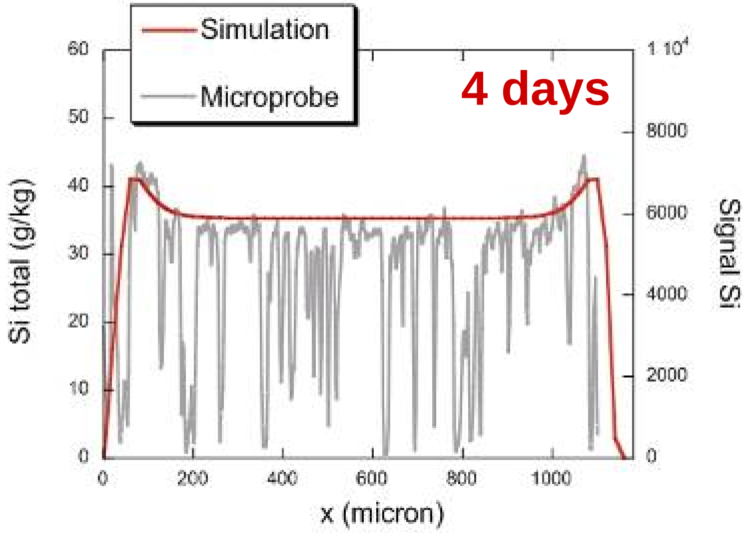


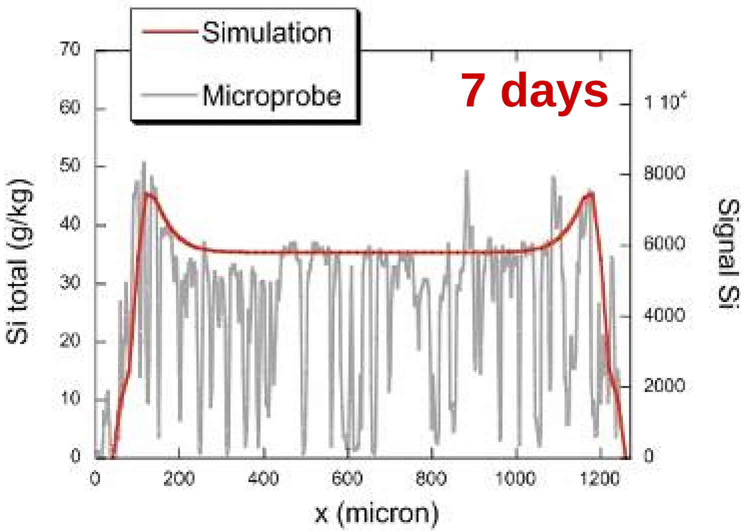
Validation - Leaching

Thin C_3S slices (w/c: 0.5) – Pure water

Silicon profiles

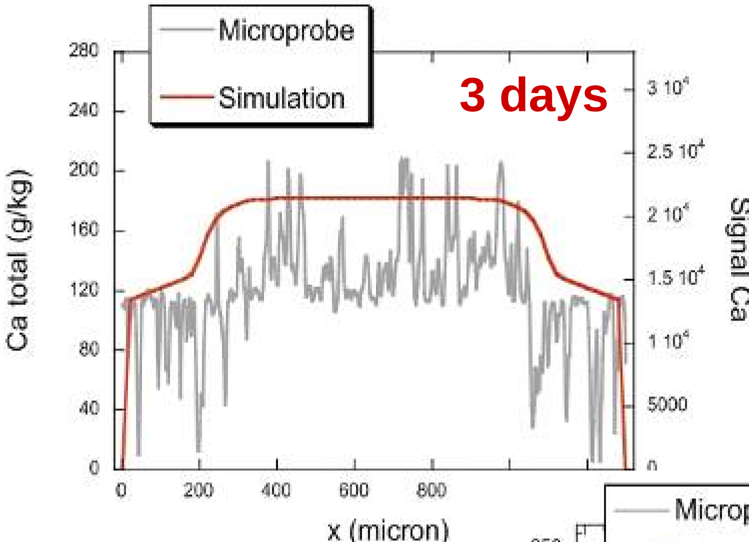


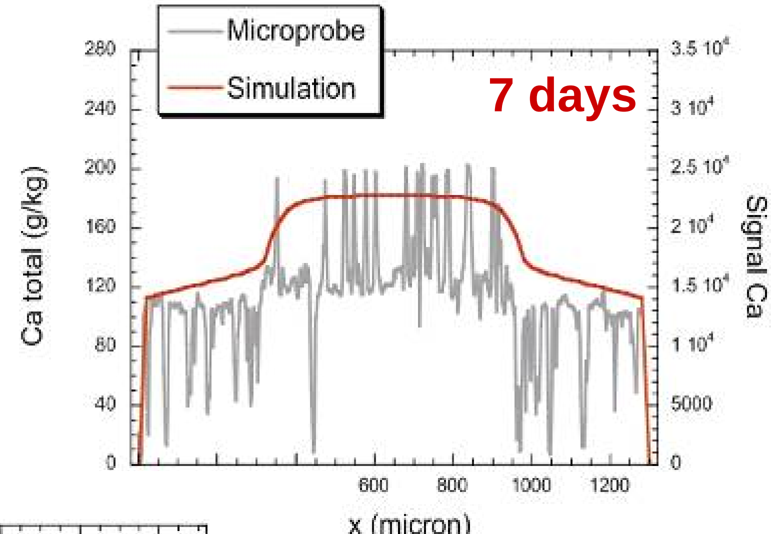


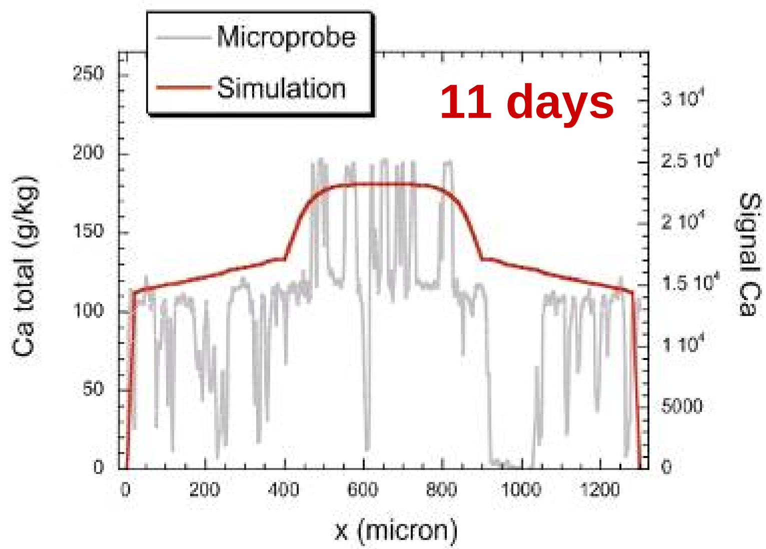


Validation – Leaching (pH = 12)

Thin C_3S slices (w/c: 0.5) - **Calcium profiles**







Validation - Leaching

Solid phase	Chemical description	Equilibrium relationship	-log(Ksp)
Portlandite	$Ca(OH)_2$	$K_{sp} = \{Ca\}\{OH\}^2$	5.2
C-S-H	$1.65CaO.SiO_2.(2.45)H_2O$ *	$K_{sp} = \{Ca\}\{OH\}^2$ **	6.2
Ettringite	$3CaO.Al_2O_3.3CaSO_4.32H_2O$	$K_{sp} = \{Ca\}^6\{OH\}^4\{SO4\}^3\{Al(OH)_4\}^2$	44.0
Monosulfates	$3CaO.Al_2O_3.CaSO_4.12H_2O$	$K_{sp} = \{Ca\}^4\{OH\}^4\{SO4\}\{Al(OH)_4\}^2$	29.1
Gypsum	$CaSO_4.2H_2O$	$K_{sp} = \{Ca\}\{SO4\}$	4.6
Mirabilite	$Na_2SO_4.10H_2O$	$K_{sp} = \{Na\}^2\{SO4\}$	1.2

{...} indicate chemical activity

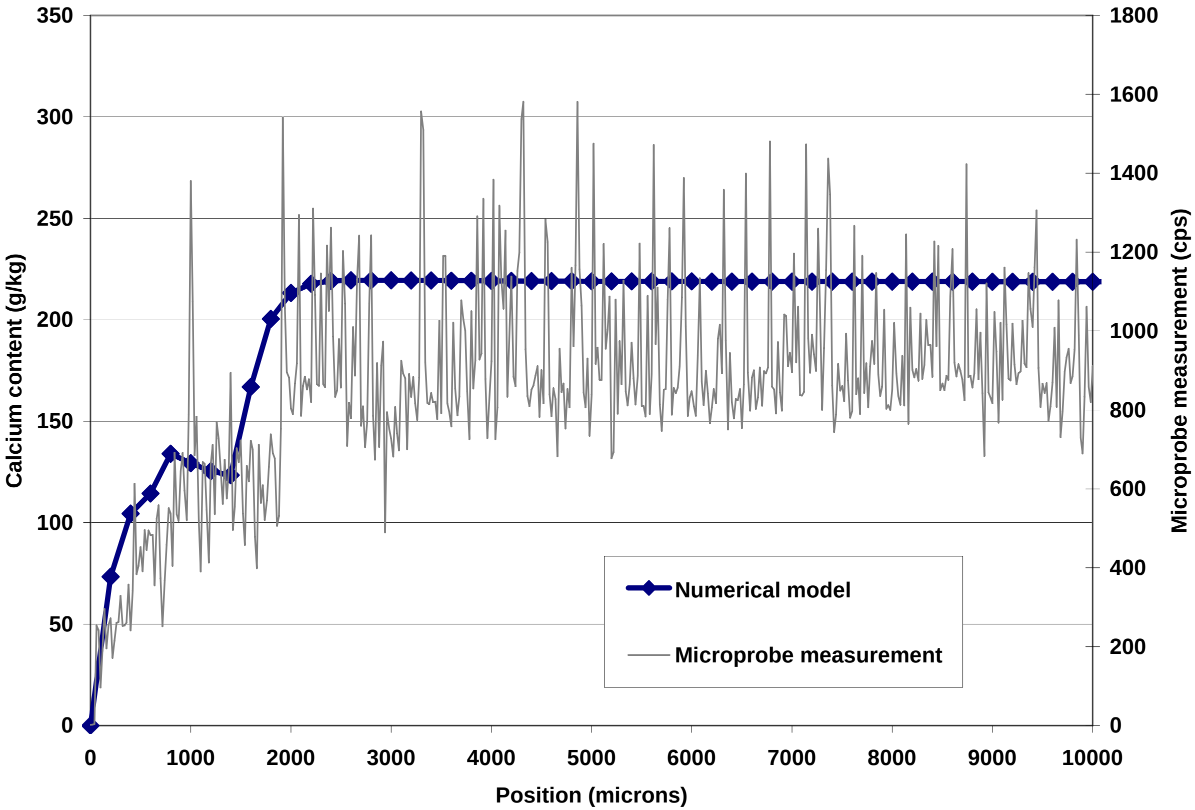
* : A C/S of 1.65 is assumed for the C-S-H

** : The C-S-H decalcification is modeled as portlandite dissolution with a lower K_{sp}

Validation - Leaching

The model has been validated for several degradation cases.

- Pure water exposure:



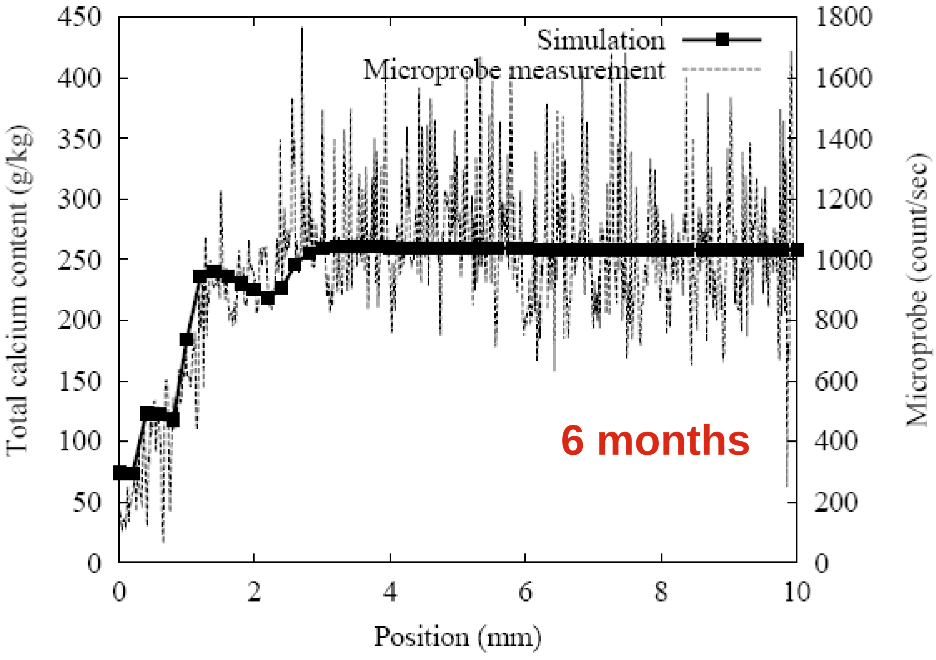
Paste (w/c:0.6, Type <u>10</u>) exposed to deionized water for 3 months –

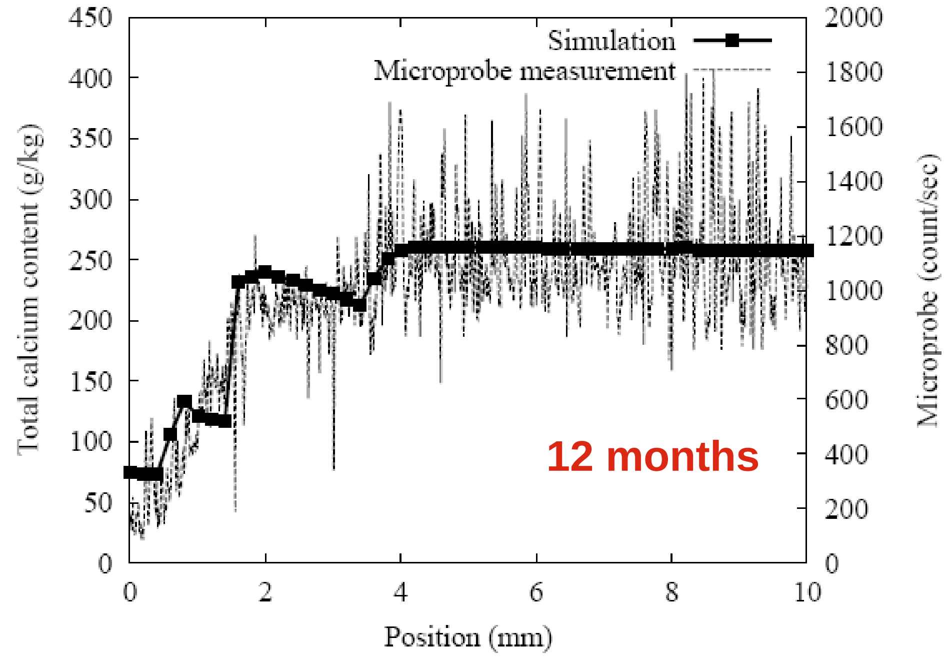
<u>Calcium profile</u>

Validation – Sulfate attack

Neat Cement Paste
(w/c: 0.6, ASTM Type I cement, Na_2SO_4 = 50 mmol/L)

Calcium profiles

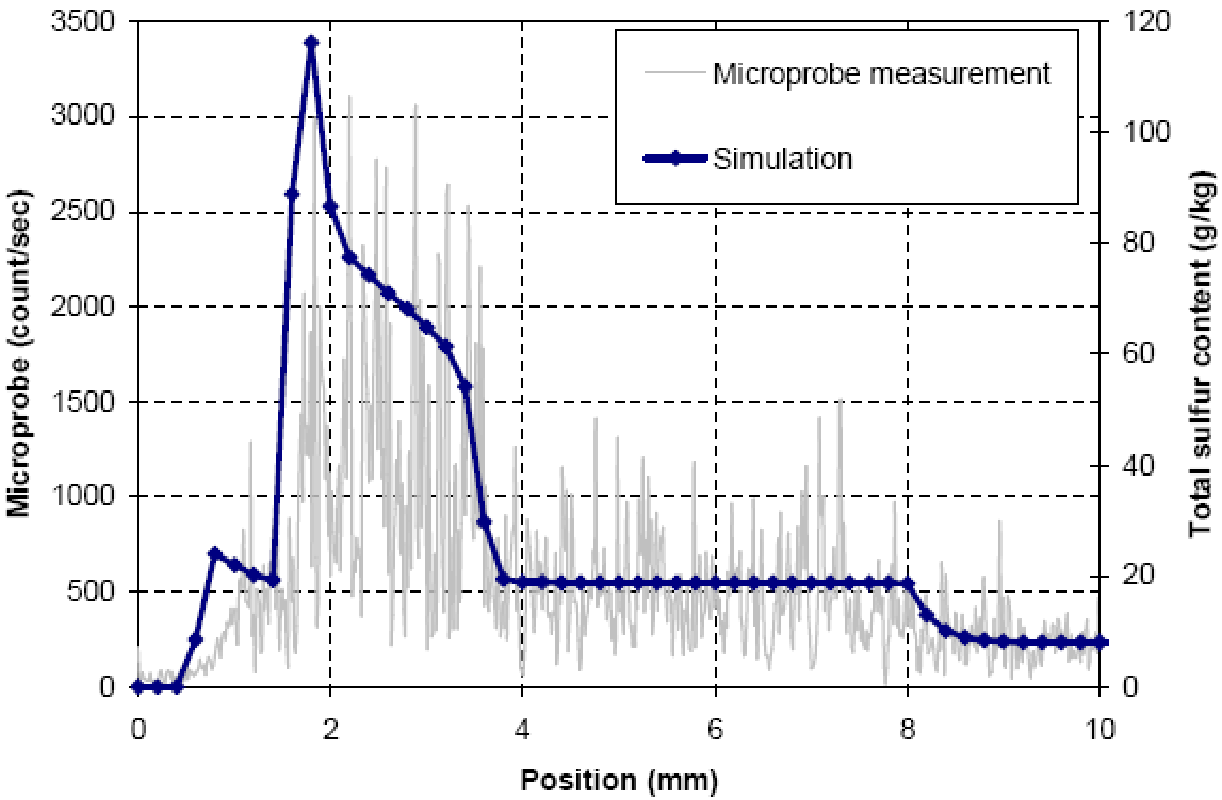




Validation – Sulfate attack

The model has been validated for several degradation cases.

- Sodium sulfate exposure:



Paste (w/c: 0.6, Type <u>10</u>) exposed to Na_2SO_4 (50 mmol/L) for 12 months –

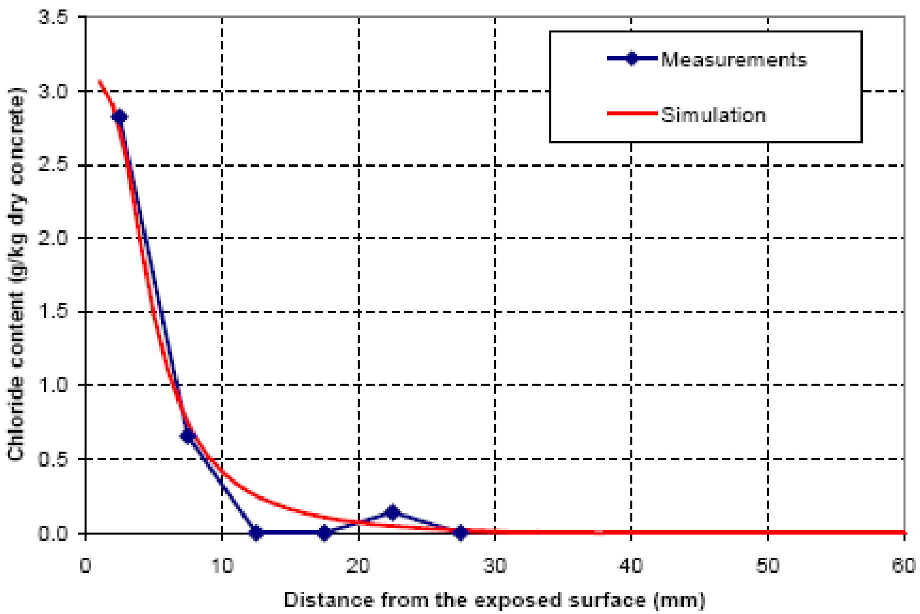
<u>Sulfur profile</u>

Validation – Chloride attack

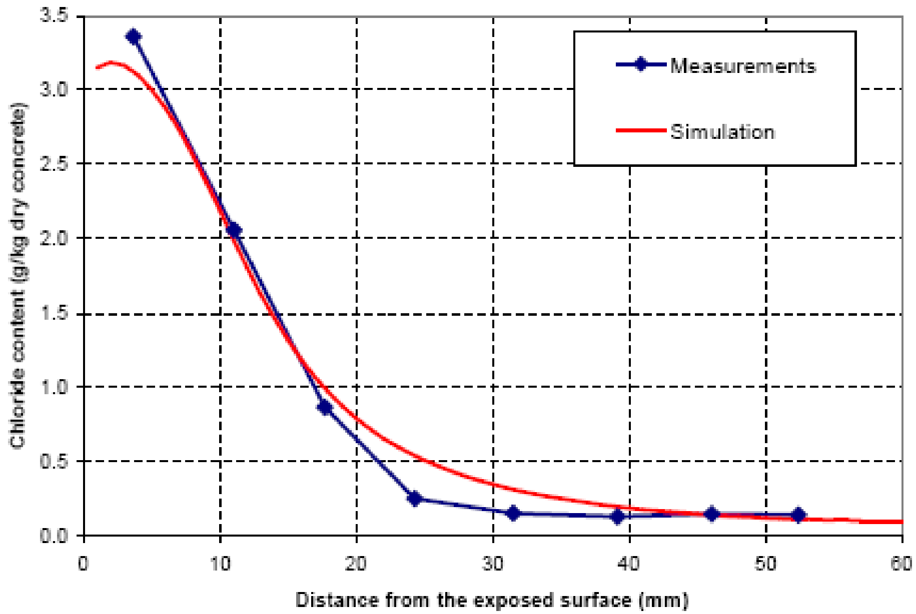
The approach has been validated for several degradation cases.

- Sodium chloride exposure:

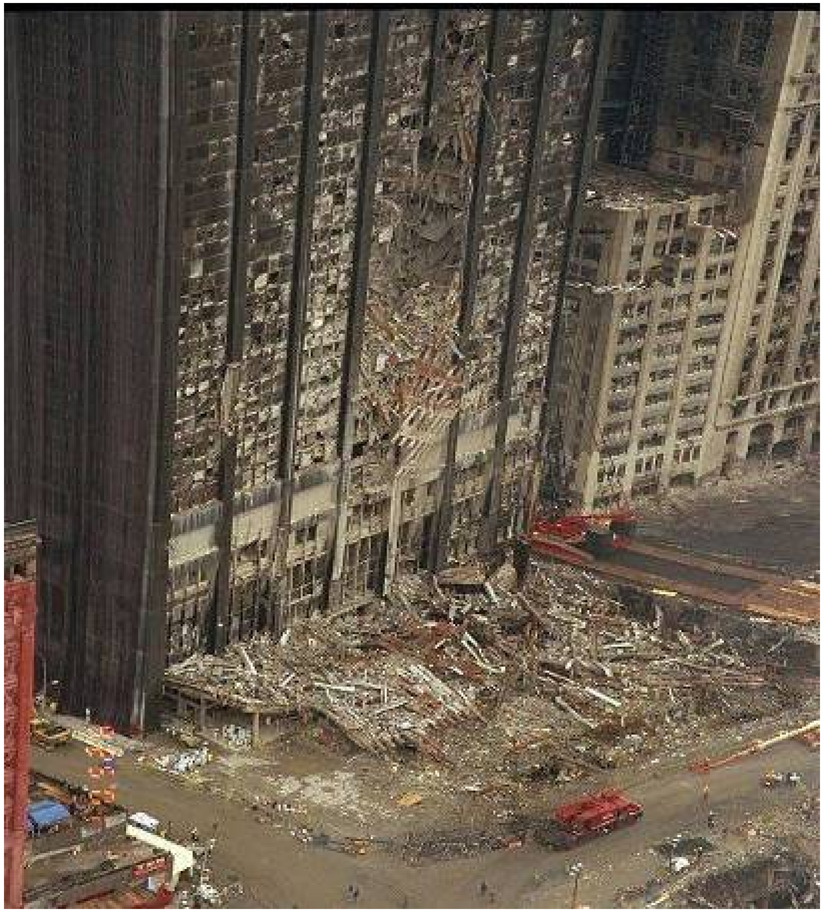
0.45 CSA Type 10 (ASTM Type I) concrete



(a) One-month exposure



(b) Eight-month exposure



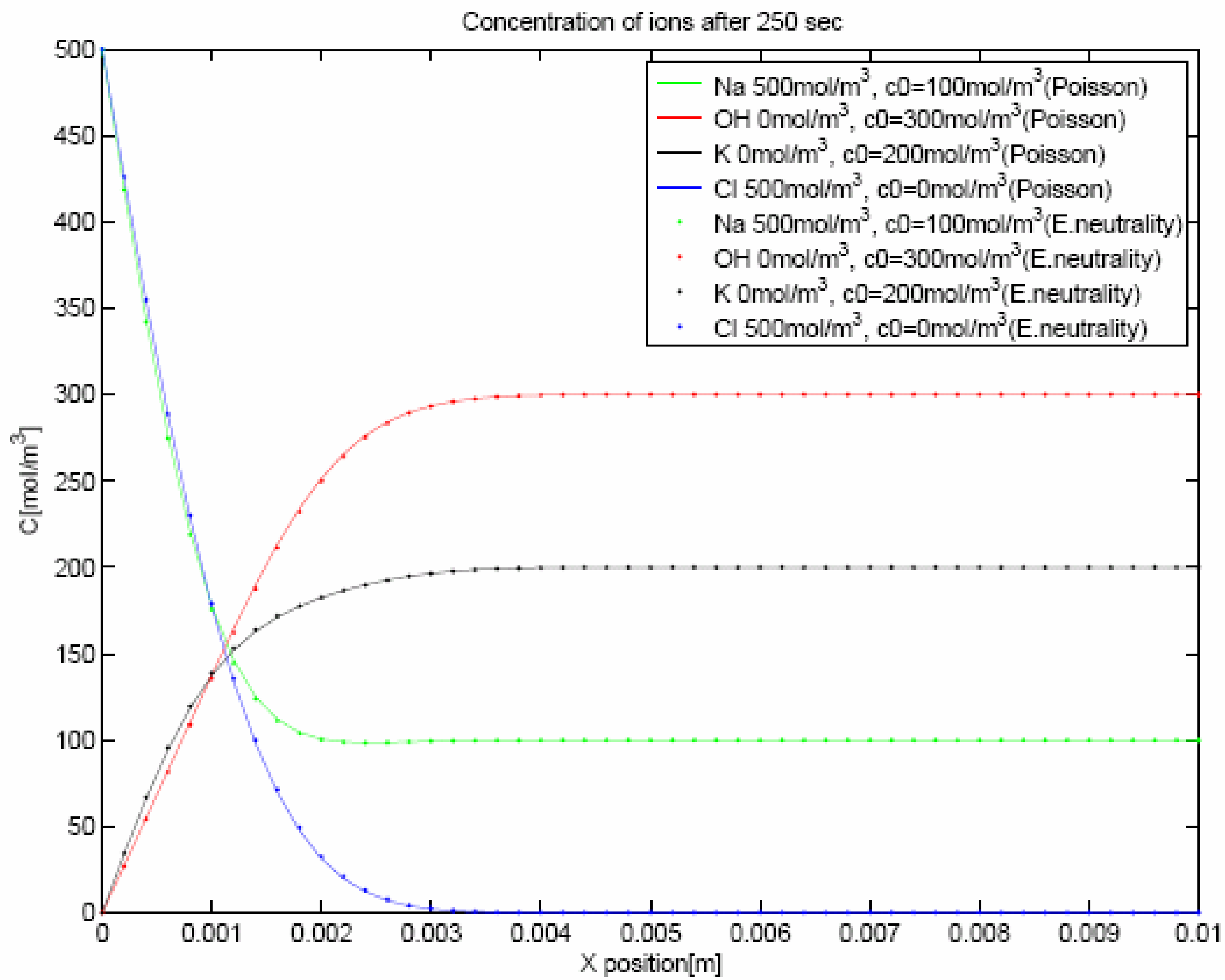
130 Liberty St. (WTC New York)

U.S. Embassy (Abu Dhabi)

Parking structure (Louisville, KY)

Questions?

Multi-ionic model



SUMMA Numerical Model for Concrete Durability

Transport properties

Modeling the effect of temperature on diffusion coefficients:

$$D_i = D_i^{ref} \exp [\alpha (T - T^{ref})]$$

Evaluation of **α**:

W/C	Hydration (days)	α (1)	
		Type 10	Type 50
0.45	28	0.0248	0.0173
	91	0.0207	0.0272
	365	0.0314	0.0377
0.65	28	0.0283	0.0277
	91	0.0372	0.0346
	365	0.0341	0.0446
0.75	28	0.0286	0.0299
	91	0.0320	0.0280
	365	0.0313	0.0309

ΣSUMMA Numerical Model for Concrete Durability

Transport properties

Modeling the effect of temperature on diffusion coefficients:

$$D_i = D_i^{ref} \exp\left[\, \alpha \,(T - T^{ref})\, \right]$$

The value of α:

- does not depend on the w/c,
- does not depend on the type of cement,
- does not depend on hydration.

The parameter α characterizes the effect of temperature on diffusion.

The global analysis of the results gives: **$\alpha = 0.028$**.

ΣSUMMA Numerical Model for Concrete Durability

Heat transfer

The following heat conduction equation is implemented in the 1D version of the model:

$$\rho C \frac{\partial T}{\partial t} - div\ \left(k \mathrm{grad} T\right) = 0$$

where the conductivity ***k*** depends on temperature ***T*** and the degree of saturation ***S*** *:

$$k = k^{ref}\left(0.244(S-1)+1\right)\times\left(0.0015\left(T-T^{ref}\right)+1\right)$$

£ **Kim et al., Cement and Concrete Research 30 (2003) 363-371**

Numerical Model for Concrete Durability

Transport equations

Without the constant temperature assumption, the following term is added to the flux relationship:

$$j_i = -D_i \frac{\partial c_i}{\partial x} - \frac{D_i z_i F}{RT} c_i \frac{\partial \psi}{\partial x} - D_i c_i \frac{\partial \ln \gamma_i}{\partial x} - \frac{D_i c_i \ln(\gamma_i c_i)}{T} \frac{\partial T}{\partial x}$$

- Special care must be taken when $c_i=0$ because of the *ln* term. Evaluating the limit shows that the term tends to 0 in that case.

ΣSUMMA
Numerical Model for Concrete Durability

Chemical reactions

The effect of temperature on chemical reactions is modeled according to the **Van’t Hoff relationship**.

It relates the equilibrium constant of the solid phases considered in **STADIUM®** with temperature.

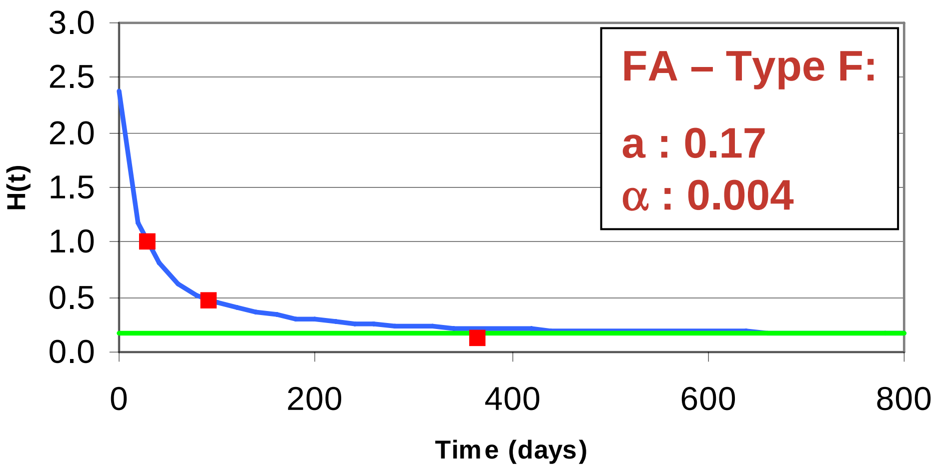
$$\ln(K_{\mathrm{sp}}) = \ln(K^o) + \frac{\Delta H^o}{R}\left(\frac{1}{T^o} - \frac{1}{T}\right)$$

- T^o and K^o are reference values at 25°C.
- ΔH^o is the reaction enthalpy.

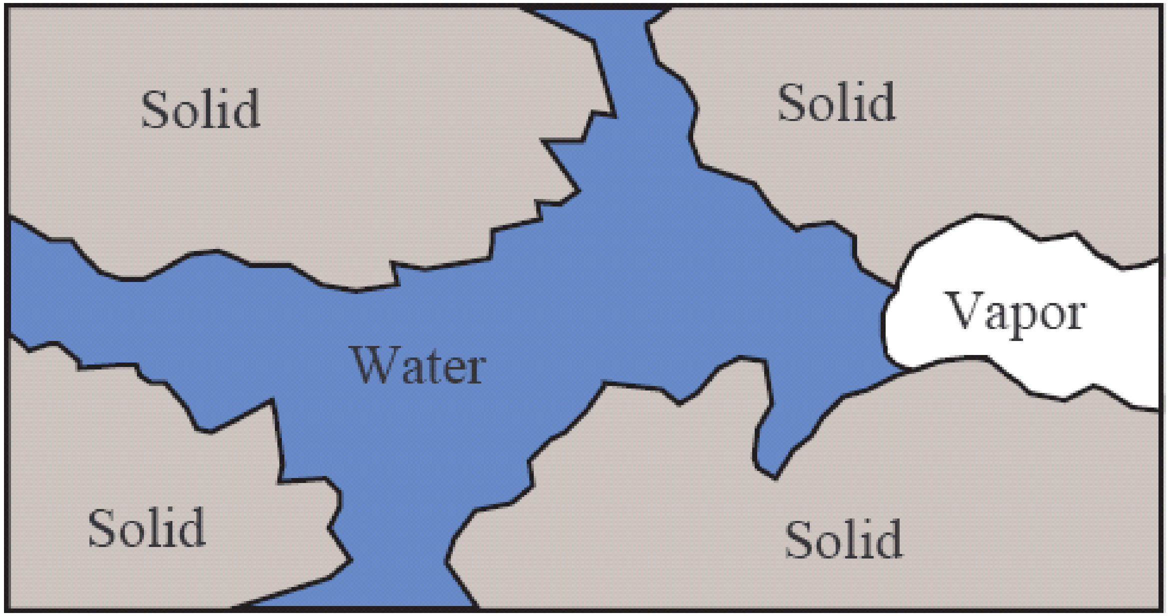
Diffusion coefficients

Hydration function: $H(t) = \dfrac{a}{1 + (a-1)e^{-\alpha(t - t_{ref})}}$

Curing	D_{Cl} (E x 10^{-11} m^2/s) Type 10
28	15,2
91	14,9
365	14,1



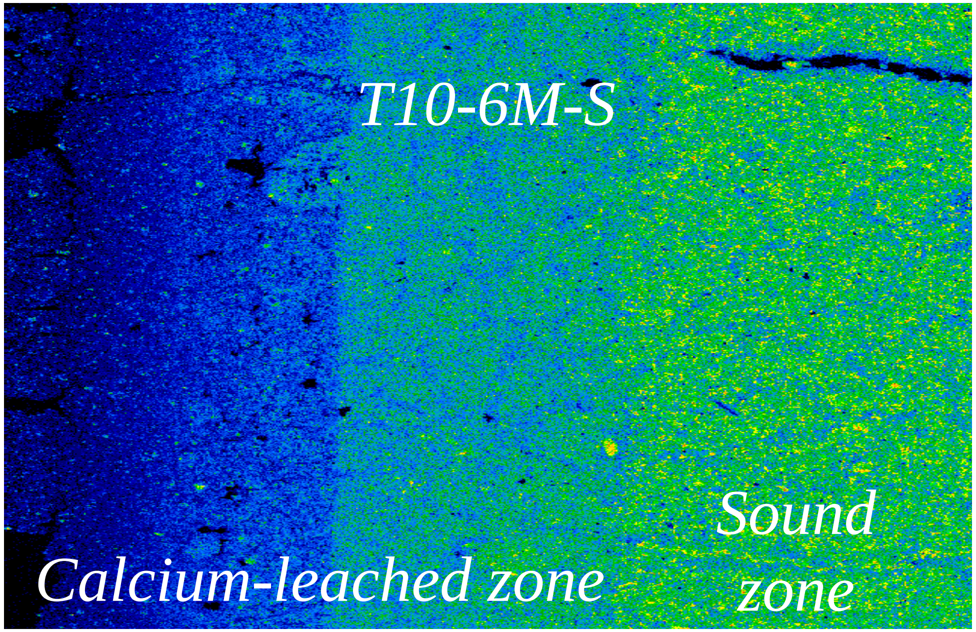
Diffusion coefficients
Impact of moisture content



$$D_i = \tau D_i^o \left(\frac{w^{7/3}}{\phi^{7/3}} \right)$$

Millington and Quirk,
Trans. Faraday Soc., vol. 57 (1961)

Diffusion coefficients
Impact of degradation



$$H_D(\phi) = \left(\frac{\phi}{\phi_o}\right)^3 \left(\frac{1-\phi_o}{1-\phi}\right)^2 \qquad H_D(\phi) = \frac{e^{4.3\phi/V_p}}{e^{4.3\phi_o/V_p}}$$

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